

7 Vapor-Liquid Equilibrium Modeling

7.1 EOS Modeling of VLE Data

(Cubic) equations of state (EOS), i.e., relations third order in molar volume between pressure, molar volume, and absolute temperature, are widely used for phase equilibrium calculations for pure fluids. The extension of equations of state from pure fluids to the prediction of phase behavior of mixtures is done using mixing and combining rules. However, the use of a single equation of state to predict the composition of both pure compounds and mixtures, in both the vapor and liquid phases, as a function of temperature and pressure, is an elusive goal. Many authors have proposed variations to the semi empirical relationship first derived by van der Waals, eqn. (4-12). One of the most successful modifications was that made by Redlich and Kwong⁵²⁹ (RK),

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5}v(v + b)}. \quad (7-1)$$

The RK equation of state has been used with good success to calculate volumetric and thermal properties of pure compounds, but its application to multicomponent vapor-liquid equilibrium (VLE) calculations often gives poor results. This has been attributed partly to the equation's lack of accuracy in expressing the influence of temperature. Soave⁵³⁰ modified the RK equation, replacing the $a/T^{0.5}$ term with a more general temperature dependent term, $a(T)$. This equation is known as the Soave -Redlich-Kwong (SRK) equation of state,

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}, \quad (7-2)$$

where

$$a(T) = \mathbf{a}(T) \cdot 0.42747 \frac{R^2 T_c^2}{P_c} \quad (7-3)$$

$$\mathbf{a}(T) = [1 + \mathbf{k}(1 - T_r^{0.5})]^2 \quad (7-4)$$

$$\mathbf{k} = 0.48508 + 1.55171\omega - 0.15613\omega^2 \quad (7-5)$$

$$b = 0.086644 \frac{RT_c}{P_c} \quad (7-6)$$

In eqns. (7-3) through (7-6), T_c , and P_c are the critical temperature and critical pressure, respectively, of the pure components, ω is the pure component acentric factor, and $T_r = T/T_c$. The SRK EOS can be written in terms of the compressibility factor, Z ,

$$Z = \frac{Pv}{RT} \quad (7-7)$$

so that

$$Z = \frac{v}{v-b} - \frac{a(T)}{RT(v+b)} \quad (7-8)$$

Kwak and Mansoori⁵³¹ suggested the replacement of the temperature dependent term $a(T)$ based on statistical-mechanical arguments and the fact that the van der Waals

mixing rules are for constants of an equation of state and not for any thermodynamic state functions that may appear in an equation of state. In order to separate thermodynamic variables from constants in the SRK equation of state, Kwak and Mansoori substitute eqns. (7-3) and (7-4) into eqn. (7-8) to obtain,

$$Z = \frac{v}{v-b} - \frac{(1 + \mathbf{k}(1 - T_r^{0.5}))^2 \left(0.42747 \frac{R^2 T_c^2}{P_c} \right)}{RT(v+b)}. \quad (7-9)$$

Expanding and rearranging terms in eqn. (7-9) gives

$$Z = \frac{v}{v-b} - \frac{1}{RT(v+b)} \left[\begin{aligned} & \left(0.42747 \frac{R^2 T_c^2}{P_c} \right) + \left(2\mathbf{k} 0.42747 \frac{R^2 T_c^2}{P_c} \right) \\ & - \left(2\mathbf{k} \left(\frac{T}{T_c} \right)^{0.5} 0.42747 \frac{R^2 T_c^2}{P_c} \right) - \left(2\mathbf{k}^2 \left(\frac{T}{T_c} \right)^{0.5} 0.42747 \frac{R^2 T_c^2}{P_c} \right) \\ & + \left(\mathbf{k}^2 0.42747 \frac{R^2 T_c^2}{P_c} \right) + \left(\mathbf{k}^2 \left(\frac{T}{T_c} \right) 0.42747 \frac{R^2 T_c^2}{P_c} \right) \end{aligned} \right] \quad (7-10)$$

$$Z = \frac{v}{v-b} - \frac{1}{(v+b)} \left[\begin{aligned} & \left[\frac{0.42747 \frac{R^2 T_c^2}{P_c}}{RT} (1 + \mathbf{k})^2 + 0.42747 \frac{R^2 T_c^2}{P_c} \left(\frac{\mathbf{k}^2}{RT_c} \right) \right] \\ & - 2 \left[\frac{0.42747 \frac{R^2 T_c^2}{P_c} (\mathbf{k}(1 + \mathbf{k}))}{RT_c^{0.5} T^{0.5}} \right] \end{aligned} \right] \quad (7-11)$$

As proposed by Kwak and Mansoori, two new terms c and d are introduced, where

$$c = 0.42747 \frac{R^2 T_c^2}{P_c} (1 + \mathbf{k})^2 \quad (7-12)$$

and

$$d = 0.42747 \frac{R^2 T_c^2}{P_c} \left(\frac{\mathbf{k}^2}{RT_c} \right) \quad (7-13)$$

so that

$$Z = \frac{v}{v-b} - \frac{c/RT + d - 2\sqrt{cd/RT}}{v+b} \quad (7-14)$$

and

$$\boxed{P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}} \quad (7-15)$$

where $a(T) = c + dRT - 2\sqrt{cdRT}$.

In this form, there are now three independent constants in the SRK equation of state: b , c , and d . These constants for the mixture are then evaluated with new mixing rules, also proposed by Kwak and Mansoori, which follow the form originally proposed by van der Waals,

$$\begin{aligned}
b &= \sum_i^n \sum_j^n x_i x_j b_{ij} , \\
c &= \sum_i^n \sum_j^n x_i x_j c_{ij} , \\
d &= \sum_i^n \sum_j^n x_i x_j d_{ij} .
\end{aligned} \tag{7-16}$$

The unlike-interaction parameters b_{ij} , c_{ij} , and d_{ij} , are determined using pure component properties and fitting parameters, k_{ij} , m_{ij} , and l_{ij} ,

$$\begin{aligned}
b_{ij} &= (1 - k_{ij}) [(b_{ii}^{1/3} + b_{jj}^{1/3}) / 2]^3 \\
c_{ij} &= (1 - l_{ij}) (c_{ii} c_{jj})^{1/2} \\
d_{ij} &= (1 - m_{ij}) [(d_{ii}^{1/3} + d_{jj}^{1/3}) / 2]^3
\end{aligned} \tag{7-17}$$

Equation (7-14) is the cubic EOS used in this work to model solvent-cosolvent vapor-liquid equilibria. In order to use eqn. (7-14) to calculate the pressure and temperature associated with a specific system volume, we need a further relationship between the volume fractions of solvent and cosolvent in the liquid and vapor phases. Various modeling procedures have been proposed in the literature to predict the phase behavior of vapor-liquid systems at high pressures. Regardless of the modeling procedure, however, the following thermodynamic relationship must be satisfied for two phases in thermodynamic equilibrium,⁵³²

$$f_i^V(T, P, y_i) = f_i^L(T, P, x_i) \tag{7-18}$$

where f_i^V is the fugacity of component i in the vapor phase, f_i^L is the fugacity of component i in the liquid phase, y_i is the mole fraction of component i in the vapor phase, and x_i is the mole fraction of component i in the liquid phase. The number of equations implied by eqn. (7-18) is equal to the number of components that appear in both the vapor and liquid phases. The fugacity of component i in each phase can now be written as

$$\begin{aligned} f_i^V(T, P, y_i) &= y_i \boldsymbol{f}_i^V P \\ f_i^L(T, P, x_i) &= x_i \boldsymbol{f}_i^L P \end{aligned} \quad (7-19)$$

where \boldsymbol{f}_i^V is the fugacity coefficient of component i in the vapor phase, P is the system pressure, T is the system temperature, and \boldsymbol{f}_i^L is the fugacity coefficient of component i in the liquid phase. Fugacity coefficients for the vapor and liquid phases are calculated from the exact thermodynamic relationships,⁵³³

$$RT \ln \boldsymbol{f}_i^V = \int_{V^V}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln Z_V \quad (7-20)$$

and

$$RT \ln \boldsymbol{f}_i^L = \int_{V^L}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln Z_L \quad (7-21)$$

where Z_V and Z_L are the mixture compressibility factors in the vapor and liquid phases, respectively.

The solution of eqn. (7-20) will be identical to that of eqn. (7-21), therefore only the solution of the vapor phase fugacity coefficient will be shown. Recalling eqn. (7-15) and substituting the quantity V/n for v (specific volume), where V is the total system volume

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V(V + nb)} \quad (7-22)$$

We next determine the partial derivative of P with respect to n , at constant T , V , and $n_{j \neq i}$.

$$\begin{aligned} \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} &= \frac{RT}{V - nb} + \frac{nRT}{(V - nb)^2} \frac{\partial(nb)}{\partial n_i} - \frac{1}{V(V + nb)} \frac{\partial(n^2 a)}{\partial n_i} \\ &+ \frac{n^2 a}{V(V + nb)^2} \frac{\partial(nb)}{\partial n_i} \end{aligned} \quad (7-23)$$

Substituting eqn. (7-23) into eqn. (7-20) or (7-21) and integrating,

$$\begin{aligned} RT \ln \mathbf{f}_i &= \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln Z, \\ &= RT \left[\ln(V - nb) \right]_V^\infty - \frac{\partial(nb)}{\partial n_i} \left[\frac{nRT}{V - nb} \right]_V^\infty + \frac{1}{nb} \frac{\partial(n^2 a)}{\partial n} \left[\ln \left(\frac{V + nb}{V} \right) \right]_V^\infty \\ &+ n^2 a \frac{\partial(nb)}{\partial n_i} \left[\left[\frac{1}{nb(V + nb)} - \frac{1}{(nb)^2} \ln \left(\frac{V + nb}{V} \right) \right] \right]_V^\infty - RT \left[\ln V \right]_V^\infty - RT \ln Z \end{aligned} \quad (7-24)$$

Evaluating the limits of integration and substituting vn for V ,

$$\begin{aligned}
RT \ln \mathbf{f}_i = & -RT \ln \left(\frac{v-b}{v} \right) + \frac{RT}{v-b} \frac{\partial(nb)}{\partial n_i} - \frac{1}{nb} \ln \left(\frac{v+b}{v} \right) \frac{\partial(n^2 a)}{\partial n_i} \\
& - \frac{a}{b} \left[\frac{1}{v+b} - \frac{1}{b} \ln \left(\frac{v+b}{v} \right) \right] \frac{\partial(nb)}{\partial n_i} - RT \ln Z
\end{aligned} \tag{7-25}$$

Simplifying, and dividing through by RT ,

$$\begin{aligned}
\ln \mathbf{f}_i = & -\ln \left(Z \left(1 - \frac{b}{v} \right) \right) - \frac{1}{nbRT} \ln \left(1 + \frac{b}{v} \right) \frac{\partial(n^2 a)}{\partial n_i} \\
& + \left[\frac{1}{v-b} - \frac{a}{bRT(v+b)} + \frac{a}{b^2 RT} \ln \left(1 + \frac{b}{v} \right) \right] \frac{\partial(nb)}{\partial n_i}
\end{aligned} \tag{7-26}$$

The last term in eqn. (7-26) can be rewritten as

$$\begin{aligned}
\left[\frac{1}{v-b} - \frac{a}{bRT(v+b)} \right] \frac{\partial(nb)}{\partial n_i} &= \frac{1}{b} \left(\frac{b}{v-b} - \frac{a}{RT(v+b)} \right) \frac{\partial(nb)}{\partial n_i} \\
&= \frac{1}{b} \left(\frac{v}{v-b} - \frac{a}{RT(v+b)} - \frac{v}{v-b} + \frac{b}{v-b} \right) \frac{\partial(nb)}{\partial n_i}
\end{aligned} \tag{7-27}$$

Substituting eqn. (7-8) into eqn. (7-27),

$$\frac{1}{b} \left(\frac{v}{v-b} - \frac{a}{RT(v+b)} - \frac{v}{v-b} + \frac{b}{v-b} \right) \frac{\partial(nb)}{\partial n_i} = \frac{1}{b} (Z-1) \frac{\partial(nb)}{\partial n_i} \tag{7-28}$$

and substituting eqn. (7-28) into eqn. (7-26),

$$\ln \mathbf{f}_i = \frac{1}{b} (Z-1) \frac{\partial(nb)}{\partial n_i} - \ln \left[Z \left(1 - \frac{b}{v} \right) \right] + \frac{a}{bRT} \left[\frac{1}{b} \frac{\partial(nb)}{\partial n_i} - \frac{1}{an} \frac{\partial(n^2 a)}{\partial n_i} \right] \ln \left(1 + \frac{b}{v} \right) \tag{7-29}$$

It is now necessary to compute the remaining derivatives in eqn. (7-29), $\left(\frac{\partial(nb)}{\partial n_i}\right)$ and

$\left(\frac{\partial(n^2a)}{\partial n_i}\right)$. Recalling the definitions given in eqn. (7-15) and eqn. (7-16),

$$\begin{aligned}\frac{\partial(nb)}{\partial n_i} &= \frac{\partial}{\partial n_i} \sum_i^n \sum_j^n x_i x_j b_{ij} = \frac{\partial}{\partial n_i} \left[\frac{1}{n} \sum_i^n \sum_j^n n_i n_j b_{ij} \right] \\ &= -\frac{1}{n^2} \sum_i \sum_j n_i n_j b_{ij} + \frac{1}{n} 2n \sum_j x_j b_{ij}\end{aligned}\quad (7-30)$$

$$\frac{\partial(nb)}{\partial n_i} = -b + 2 \sum_j^n x_j b_{ij}$$

$$\frac{\partial(n^2a)}{\partial n_i}\quad (7-31)$$

$$\frac{\partial(n^2a)}{\partial n_i} = \frac{\partial(n^2c)}{\partial n_i} + RT \frac{\partial(n^2d)}{\partial n_i} - 2\sqrt{RT} \frac{\partial[(n^2cn^2d)^{1/2}]}{\partial n_i}$$

where, as before $a = c + dRT - 2\sqrt{cdRT}$. Similarly for the derivatives $\left(\frac{\partial(n^2c)}{\partial n_i}\right)$,

$$\left(\frac{\partial(n^2d)}{\partial n_i}\right), \text{ and } \left(\frac{\partial(\sqrt{n^2cn^2d})}{\partial n_i}\right),$$

$$\frac{\partial(n^2c)}{\partial n_i} = \frac{\partial}{\partial n_i} n^2 \sum_i^n \sum_j^n x_i x_j c_{ij} = \frac{\partial}{\partial n_i} \sum_i^n \sum_i^n n_i n_j c_{ij} = 2 \sum_j^n n_j c_{ij} = 2n \sum_j^n x_j c_{ij} \quad (7-32)$$

$$\frac{\partial(n^2 d)}{\partial n_i} = 2n \sum_j^n x_j d_{ij}, \quad (7-33)$$

$$\begin{aligned} \frac{\partial}{\partial n_i} \left[\sqrt{n^2 c} \sqrt{n^2 d} \right] &= \frac{\sqrt{n^2 d}}{2\sqrt{n^2 c}} \frac{\partial(n^2 c)}{\partial n_i} + \frac{\sqrt{n^2 c}}{2\sqrt{n^2 d}} \frac{\partial(n^2 d)}{\partial n_i} \\ &= \frac{1}{2} \sqrt{\frac{d}{c}} \left(2n \sum_j^n x_j c_{ij} \right) + \frac{1}{2} \sqrt{\frac{c}{d}} \left(2n \sum_j^n x_j d_{ij} \right) = n \sqrt{\frac{d}{c}} \left(\sum_j^n x_j c_{ij} \right) + n \sqrt{\frac{c}{d}} \left(\sum_j^n x_j d_{ij} \right) \end{aligned} \quad (7-34)$$

Substituting eqns. (7-32) to (7-34) back into eqn. (7-31) and simplifying,

$$\frac{\partial(n^2 a)}{\partial n_i} = 2n \left[\sum_j^n x_j c_{ij} + RT \sum_j^n x_j d_{ij} - \sqrt{RT} \left(\sqrt{\frac{d}{c}} \sum_j^n x_j c_{ij} + \sqrt{\frac{c}{d}} \sum_j^n x_j d_{ij} \right) \right] \quad (7-35)$$

Substituting eqns. (7-35) and (7-30) into eqn. (7-29),

$$\begin{aligned} \ln f_i &= \frac{1}{b} (Z - 1) \left(-b + 2 \sum_j^n x_j b_{ij} \right) - \ln \left[Z \left(1 - \frac{b}{v} \right) \right] + \frac{a}{bRT} \left[\frac{1}{b} \left(-b + 2 \sum_j^n x_j b_{ij} \right) \ln \left(1 + \frac{b}{v} \right) \right] \\ &\quad - \frac{a}{bRT} \left[\frac{1}{an} 2n \left(\sum_j^n x_j c_{ij} + RT \sum_j^n x_j d_{ij} - \sqrt{RT} \left(\sqrt{\frac{d}{c}} \sum_j^n x_j c_{ij} + \sqrt{\frac{c}{d}} \sum_j^n x_j d_{ij} \right) \right) \right] \ln \left(1 + \frac{b}{v} \right) \end{aligned} \quad (7-36)$$

Finally, making the substitutions, $v = \frac{ZRT}{P}$ and $B = \frac{bP}{RT}$, eqn. (7-36) simplifies to

$$\ln f_i = \left[\left(\frac{2}{b} \sum_j x_j b_{ij} \right) - 1 \right] \left[Z - 1 + \frac{a}{bRT} \ln \left(1 + \frac{B}{Z} \right) \right] - \ln(Z - B) - \frac{2}{bRT} \ln \left(1 + \frac{B}{Z} \right) \left[\sum_j x_j c_{ij} + RT \sum_j x_j d_{ij} - \sqrt{RT} \left(\sqrt{\frac{d}{c}} \sum_j x_j c_{ij} + \sqrt{\frac{c}{d}} \sum_j x_j d_{ij} \right) \right]$$

(7-37)

Equation (7-37) is applicable to both the vapor and liquid phase fugacity coefficients with the appropriate vapor or liquid phase values used. Equations for b , c , and d are as defined earlier (again these equations are solved separately for the vapor phase and a liquid phase). Calculation of the compressibility factor, Z , is from the polynomial form of the SRK equation,

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (7-38)$$

where

$$A = \frac{aP}{R^2 T^2} \quad (7-39)$$

$$B = \frac{bP}{RT}.$$

and $a = c + dRT - 2\sqrt{cdRT}$.

Solving eqn. (7-38) results in three roots. The largest positive root corresponds to the fugacity coefficient of the vapor phase, while the smallest positive root corresponds to the fugacity coefficient of the liquid phase.⁵³⁴ The intermediate root is discarded.

$$y_i \mathbf{f}_i^V P = x_i \mathbf{f}_i^L P, \quad (7-40)$$

$$\therefore y_{i,calc} = \frac{x_{i,exp} \mathbf{f}_i^L}{\mathbf{f}_i^V}, \quad \text{and} \quad x_{i,calc} = \frac{y_{i,exp} \mathbf{f}_i^V}{\mathbf{f}_i^L}.$$

7.2 Example: CO₂-Propylene Carbonate System

Propylene carbonate is a polar solvent used at the Supercritical; Fluids Facility as a co-solvent for polymer removal.^{535,536} The use of the SRK EOS will be illustrated by modeling some newly acquired vapor-liquid equilibrium (VLE) data. The new isothermal vapor-liquid equilibrium data was measured at 298.15 K, 308.15 K, 333.15 K and 373.15 K over a pressure range from 41 to 206.8 bars.⁵³⁷ The results are listed in Table 7-1, where x_2 and y_2 are the mole fractions of carbon dioxide in the liquid phase and vapor phase, respectively.

Table 7-1. Experimental vapor-liquid equilibrium data for propylene carbonate (1) - carbon dioxide (2) mixtures.

T (K)	P (bar)	x_2	y_2	T (K)	P (bar)	x_2	y_2
298.15	41.37	0.4373	0.99999	333.15	137.90	0.6161	0.99394
298.15	61.24	0.7091	0.99989	333.15	172.37	0.6737	0.98522
308.15	55.16	0.4788	0.99995	333.15	206.84	0.7318	0.97279
308.15	82.74	0.6774	0.99381	373.15	55.16	0.2122	0.99953
308.15	110.32	0.7234	0.98665	373.15	82.74	0.2989	0.99917
308.15	137.90	0.7608	0.98281	373.15	110.32	0.3720	0.99852
333.15	55.16	0.3313	0.99990	373.15	137.90	0.4366	0.99776
333.15	82.74	0.4577	0.99958	373.15	172.37	0.5043	0.99542
333.15	110.32	0.5558	0.99855	373.15	206.84	0.5559	0.99152

The experimental phase equilibrium data obtained were modeled using the SRK EOS as described in Section 7.1. The critical constants, T_C , P_C , and acentric factor, ω , of the pure components, for use in eqns. (7-3) through (7-6), are summarized in Table 7-2.

Table 7-2. Critical properties and acentric factors of pure components.

Component	T _c (K)	P _c (bar)	w
Propylene Carbonate ⁵³⁸	625.15	57.05	.707 ⁵³⁹
Carbon Dioxide ⁵⁴⁰	304.1	73.8	.239

The experimental data in Table 7-1 was fit using an objection function, eqn. (7-41), which minimizes the difference between the experimental CO₂-propylene carbonate vapor and liquid mole fractions and the same mole fractions calculated as described in Section 7.1.

$$\min(S) = \sum (y_{\text{exp}} - y_{\text{calc}})^2 + \sum (x_{\text{exp}} - x_{\text{calc}})^2 \quad (7-41)$$

The values obtained for the three binary fitting parameters, eqn. (7-17), are

$$\begin{aligned} k_{ij} &= -0.041 \\ l_{ij} &= -0.115 \\ m_{ij} &= -0.063 \end{aligned}$$

The results of the modeling correlation are shown in Figure 7-1. The solid lines represent the isotherms calculated using the interaction parameters k_{ij} , l_{ij} , and m_{ij} obtained from the correlation. It can be seen that the agreement is quite good for both the liquid and vapor phases, especially at the higher temperatures.

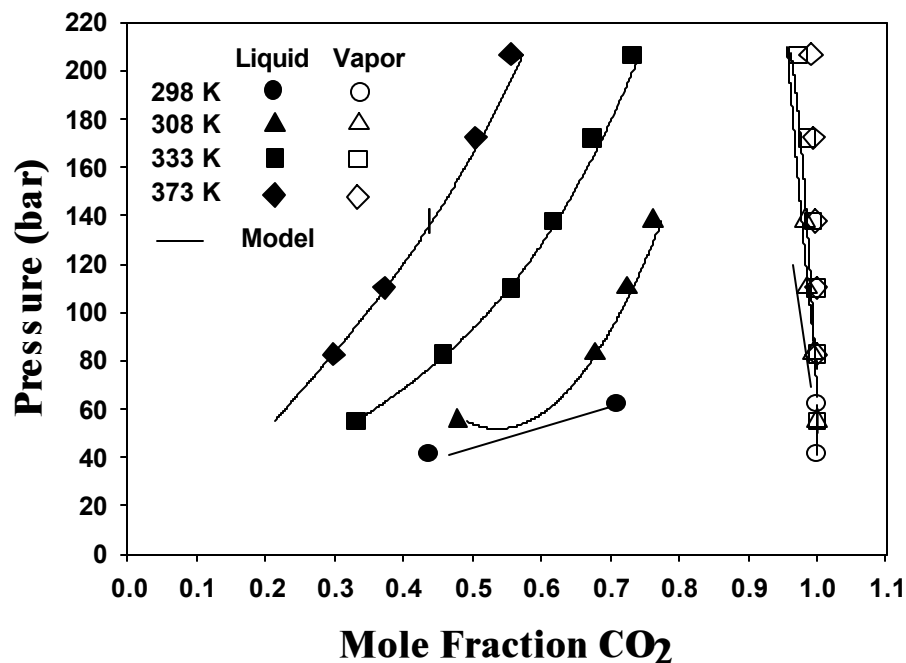


Figure 7-1. Experimental data and results of VLE modeling of the propylene carbonate-CO₂ system.

Figure 7-2 shows that the high-pressure experimental range in this work and in existing literature. It is seen that the experimental data has been extended into the pressure range useful for supercritical CO₂ processing. All the propylene carbonate/CO₂ VLE data^{541,542} (this work, as well indicated references) were modeled using the previously calculated interaction parameters k_{ij} , l_{ij} , and m_{ij} , and results of the liquid equilibrium correlation are represented by the solid lines in Figure 7-2. Again, good agreement is seen between the experimental and calculated values.

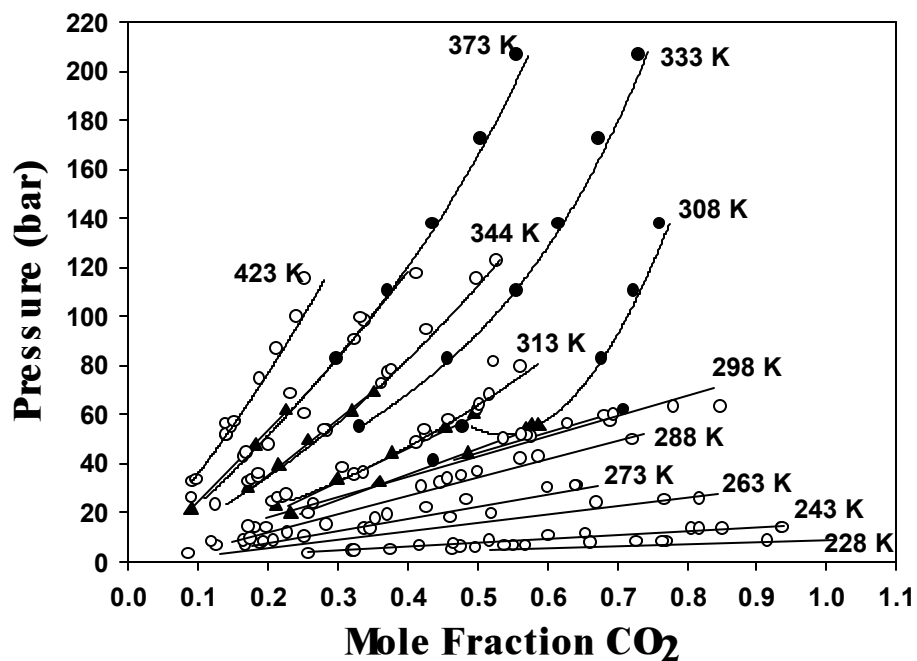


Figure 7-2. Comparison of high-pressure propylene carbonate- CO_2 VLE. This work - - ; reference 543 \blacktriangle ; reference 544 \circ .

A similar modeling procedure was performed for existing vapor-liquid equilibrium data for carbon dioxide-ester binary systems. As in the previous analysis, the correlation utilized three interaction parameters and minimized the difference between the experimental and calculated CO_2 -ester mole fractions. These parameter values and the source of the experimental CO_2 /ester VLE data are shown in Table 7-3 .

Table 7-3. Results of VLE modeling of carbon dioxide(2) + ester(1) binary systems.

Component 1	Chemical Formula P_v^a	No. points	T (°C)	P (bar)	Ref.	k_{ij}	l_{ij}	m_{ij}	Sum of squares, $\Sigma\Delta x$, and AAD**
methyl acetate	$\text{CH}_3\text{COOCH}_3$ ($P_v = 0.29$ bar)	22	298.15 - 313.15	6.5 - 80	545	-0.204	-0.025	0.176	0.0011 0.0065
ethyl acetate	$\text{CH}_3\text{CH}_2\text{COOCH}_3$ ($P_v = 0.12$ bar)	42	303.15 - 323.15	20 - 90	546	-0.371	-0.216	0.015	0.0112 0.0138
propyl acetate	$\text{CH}_3(\text{CH}_2)_2\text{COOCH}_3$ ($P_v = 0.05$ bar)	56	303.15 - 323.15	20 - 92	547	-0.338	-0.130	0.150	0.0093 0.0108
ethyl propanoate	$\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ ($P_v = 0.05$ bar)	74	303.15 - 323.15	17 - 92	548	-0.245	-0.096	0.121	0.0093 0.0086
methyl myristate	$\text{CH}_3(\text{CH}_2)_{12}\text{COOCH}_3$ ($P_v = 0.004$ bar)	17	313.15 - 343.15	72 - 160	549	-0.393	-0.066	0.343	0.0003 0.0042
methyl palmitate	$\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3$ ($P_v = 0.002$ bar)	25	313.15 - 343.15	62 - 183	“	-0.453	0.056	0.530	0.0002 0.0023
methyl oleate	$\text{CH}_3(\text{CH}_2)_7(\text{CH})_2(\text{CH}_2)_7\text{COOCH}_3$ ($P_v = 0.0004$ bar)	25	313.15 - 343.15	72 - 200	“	-0.455	0.062	0.557	0.0010 0.0033
methyl stearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$ ($P_v = 0.0005$ bar)	22	313.15 - 343.15	60 - 198	“	-0.472	-0.040	0.451	0.0007 0.0045
propylene carbonate	$\text{CH}_3\text{CH}_2\text{OCOO}$ ($P_v = 0.00006$ bar)	18	298.15 - 373.15	41 - 207	b	-0.041	-0.115	-0.063	0.0021 0.0081

^a Vapor pressure at atmospheric conditions, bars.

^b This work